# POLARIZATION OF FLUORESCENCE:  A PROBE OF MOLECULAR AUTOIONIZATION*

G. E. Leroi

Michigan State University, East Lansing, MI 48824 USA

J. L. Dehmer

Argonne National Laboratory, Argonne, IL 60439 USA

A. C. Parr

National Bureau of Standards, Washington, DC 20234 USA

E. D.  Poliakoff

Boston University, Boston, MA 02215 USA

## ABSTRACT
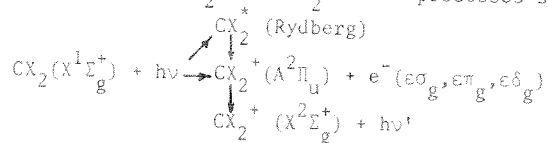
The polarization of fluorescence from excited-state molecular photoions  provides a direct probe of the photoionization dynamics and the symmetry signatures of autoionizing resonances. Measurements on $CO_2$ and $CS_2$ are presented as examples.

The polarization of fluorescence from excited-state molecular photoions provides a direct measure of their alignment, and thus the relative dipole strength of degenerate excitation channels.[1,2]  Hence fluorescence polarization can be used to characterize the symmetry signatures and dynamical properties of autoionizing resonances.[3]  We report here the excitation wavelength dependence of the polarization of $A^2\Pi_u \rightarrow X^2\Pi_g$ fluorescence from $CO_2^+$ and $CS_2^+$.  The processes studied are represented below:

$$CX_2(X^1\Sigma_g^+) + h\nu \nearrow \begin{array}{c} CX_2^* \text{ (Rydberg)} \\ \downarrow \\ CX_2^+(A^2\Pi_u) + e^-(\epsilon\sigma_g,\epsilon\pi_g,\epsilon\delta_g) \\ \downarrow \\ CX_2^+(X^2\Sigma_g^+) + h\nu' \end{array}$$

Here $CX_2$ is either $CO_2$ or $CS_2$, and $\epsilon$ denotes a continuum electron.

In the experiments, monochromatic VUV radiation (0.8Å bandwidth) from SURF-II (Synchrotron Ultraviolet Radiation Facility at the U.S. National Bureau of Standards) impinged on the gas sample which expanded from an effusive jet.  At each excitation wavelength, undispersed fluorescence ($h\nu'$) at $90°$ was collected by a planoconvex lens, passed through a polarizer rotated under computer control, and detected by a thermoelectrically cooled photomultiplier.  The data were corrected for instrumental effects and the incomplete polarization of the incident radiation.  Excitation spectra were obtained with the polarizer removed.

The results for $CO_2$ are shown in Fig. 1. The excitation spectrum (bottom frame) shows extensive autoionization structure and is in good agreement with previous work.[4,5] The corrected fluorescence polarization spectrum ($P_{fl}$, top frame) shows analogous structure, superimposed on a non-resonant background for which $P_{fl} \approx -0.07\pm0.01$. Theoretical work[6,7] indicates that $1\pi_u \to \varepsilon\delta_g$ photoionization is the dominant nonresonant excitation channel near the A-state threshold for $CO_2$, and the experimental result is consistent with the polarization calculated[2] upon that expectation: $P_{fl} = -0.077$. This value arises because the absorption transition dipole is perpendicular to the internuclear axis, whereas the fluorescence transition dipole is parallel to that axis.[2]
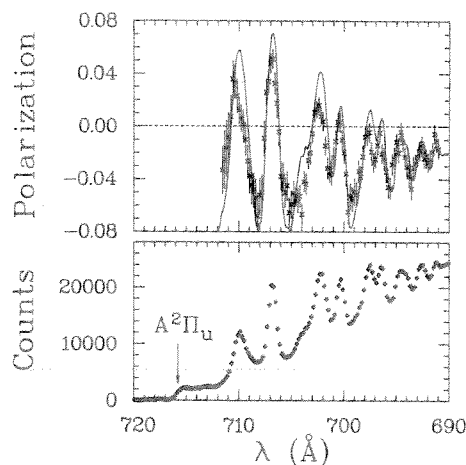
Fig. 1. *Excitation spectrum (bottom) and corrected polarization profile (top) for A→X fluorescence from $CO_2$. The solid line is $P_{fl}$ predicted by a simple mixing model.*

The symmetry of the autoionizing Rydberg states will also determine the fluorescence profile in the regions of resonant excitation. There has been some ambiguity regarding the symmetry assignments in this spectral region,[8,9] but we obtain rather good agreement with the polarization data if we assume that *each* resonant feature emanates from a $^1\Sigma_u^+$ Rydberg state. In this case the transition dipoles are parallel to the intermolecular axis for both absorption and fluorescence, leading to $P_{fl} = +0.143$ for the resonant contributions.[2] (Rydberg states with $^1\Pi_u$ symmetry lead to $P_{fl} = -0.077$, like the nonresonant background.) Hence, these results contradict an earlier assignment[9] of the 707Å peak as $^1\Pi_u$. The solid line in the top frame of Fig. 1 represents the $P_{fl}$ predicted from the excitation spectrum, based on a simple weighted average of resonant and nonresonant contributions at each wavelength.

For $CS_2$ several autoionizing Rydberg series which converge to the B-state of the ion have been identified.[10,11] A small portion of the fluorescence excitation spectrum (bottom) and the corresponding polarization profile (top) are shown in Fig. 2. The polarization behavior shows clearly that the two resonance features in
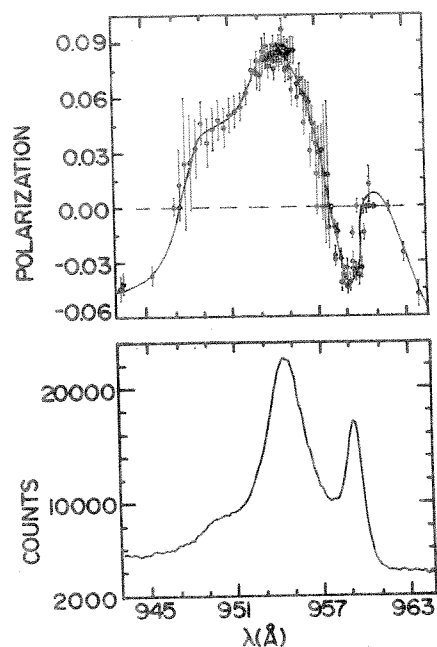
Fig. 2. *Portion of the excitation (bottom) and polarization (top) spectra for A→X fluorescence from $CS_2^+$. [The line through the data points is a guide to the eye, only.]*

the excitation spectrum belong to states with *different* symmetry. The stronger peak contributes the positive $P_{fl}$ expected from a $\Sigma$ state; however, the sharp decrease in $P_{fl}$ at the longer wavelength peak reflects a Rydberg state of $\Pi$ symmetry. Other members of the latter series are similarly distinguished elsewhere in the polarization spectrum.

These results demonstrate that the alignment of an excited molecular ion in the laboratory frame, which is dependent on the dipole strengths of the competing ionization channels, is reflected in the fluorescence polarization data. Polarization of fluorescence from excited photoions yields spectroscopic and dynamical information about resonant and nonresonant excitation pathways *directly*, thus complementing existing probes of molecular photoionization.

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